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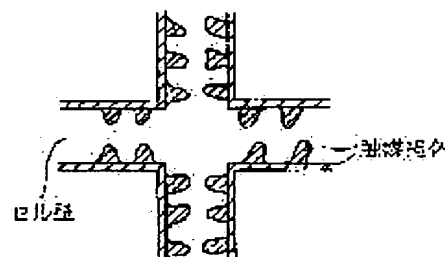
(54) CATALYST CARRIER STRUCTURE BODY AND CATALYST FOR CLEANING EXHAUST GAS

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a catalyst for cleaning an exhaust gas with high durability in which a pressure loss of the exhaust gas is low and an exhaust gas cleaning performance is high.

**SOLUTION:** A circulation type catalyst carrier structure body is used for the catalyst for cleaning the exhaust gas and in the structure body and keeps a honeycomb base material coated with a catalyst carrier. A cell wall pore of the honeycomb base material and a cell wall surface are coated with the catalyst carrier. An amount of the catalyst carrier coating the cell wall surface is 10-40% by mass of the whole catalyst carrier and the coating layer of the catalyst carrier on the cell wall surface has a thickness less than 100  $\mu\text{m}$ . The catalyst carrier coating the cell wall surface can be only positioned at a downstream side of the exhaust gas. The catalyst for cleaning the exhaust gas is constituted by making such a catalyst carrier structure body carry at least one kind of noble metal selected from Pt, Pd and Rh on.

図1 本発明の触媒担持構造体のモデル図



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CLAIMS

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[Claim(s)]

[Claim 1] The catalyst support structure which it is used for the catalyst for exhaust gas clarification, and it is the catalyst support structure of the negotiation type which comes to carry out the coat of the catalyst support to a honeycomb base material, and the coat of the catalyst support is carried out the inside of the cell wall pore of a honeycomb base material, and on a cell wall front face, and is characterized by for the amount of the catalyst support on the cell wall front face by which the coat was carried out being ten to 40 mass [ of the whole catalyst support ] %, and the coat layer of the catalyst support on a cell wall front face being the thickness of less than 100 micrometers.

[Claim 2] The catalyst support structure according to claim 1 whose coat layer of the catalyst support on a cell wall front face the amount of the catalyst support on the cell wall front face by which the coat was carried out is ten to 30 mass [ of the whole catalyst support ] %, and is the thickness of less than 70 micrometers.

[Claim 3] It is the catalyst support structure of the negotiation type which it is used for the catalyst for exhaust gas clarification, and comes to carry out the coat of the catalyst support to a honeycomb base material. The coat of the catalyst support is carried out the inside of the cell wall pore of a honeycomb base material, and on a cell wall front face, and it sets to the exhaust gas downstream of the catalyst support structure. The amount of the catalyst support on the cell wall front face by which the coat was carried out is ten to 40 mass [ of the whole catalyst support ] %, and the coat layer of the catalyst support on a cell wall front face is less than 100 micrometers in thickness, and it sets to the exhaust gas upstream of the catalyst support structure. The catalyst support structure to which the amount of the catalyst support in the cell wall pore by which the coat was carried out is characterized by being more than 90 mass % of the whole catalyst support.

[Claim 4] The catalyst support structure according to claim 3 whose coat layer of the catalyst support on a cell wall front face the amount of the catalyst support on the cell wall front face by which the coat was carried out is ten to 30 mass [ of the whole catalyst support ] % in the exhaust gas downstream of the catalyst support structure, and is the thickness of less than 70 micrometers.

[Claim 5] The catalyst support structure given in any 1 term of claims 1-4 in which the cell wall of a honeycomb base material has 40 - 75% of porosity, and D50 pore diameter of 10-50 micrometers.

[Claim 6] The catalyst support structure given in any 1 term of claims 1-5 whose catalyst support is at least one sort chosen from alumina, zirconia, Seria, zirconia-Seria, and alumina-Seria-zirconia and Seria-zirconia-yttria and zirconia-calcia.

[Claim 7] The catalyst support structure given in any 1 term of claims 1-6 whose pores of the cell wall of a honeycomb base material are non-breakthroughs substantially.

[Claim 8] The catalyst for exhaust gas clarification which is a catalyst for exhaust gas clarification with which the catalyst support structure given in any 1 term of claims 1-7 comes to support a catalyst component, and is characterized by the catalyst component supported by the catalyst support in cell wall pore and the catalyst component supported by the catalyst support on a cell wall front face being substantially different.

[Claim 9] The catalyst for exhaust gas clarification according to claim 8 with which NO<sub>x</sub> occlusion material was supported by the catalyst support in cell wall pore, and at least one sort of noble metals chosen as the catalyst support on a cell wall front face from Pt, Pd, and Rh were supported.

[Claim 10] The catalyst for exhaust gas clarification according to claim 8 with which Pt and/or Pd were supported by the catalyst support in cell wall pore, and Rh was supported by the catalyst support on a cell wall front face.

[Claim 11] The manufacture approach of the catalyst support structure given in any 1 term of claims 1-7 characterized by carrying out the coat of the catalyst support on the cell wall front face of a honeycomb base material using the slurry containing ceramic fiber after carrying out the coat of the catalyst support into the cell wall pore of a honeycomb base material.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the catalyst support structure of a negotiation type, and the catalyst for exhaust gas clarification, this invention is divided and relates to the catalyst support structure for purifying efficiently the exhaust gas discharged by internal combustion engines, such as car motor, by low pressure loss, and the catalyst for exhaust gas clarification.

[0002]

[Description of the Prior Art] A carbon monoxide (CO), a hydrocarbon (HC), nitrogen oxides (NOX), etc. are contained in the exhaust gas discharged by internal combustion engines, such as car motor, and, generally such harmful matter is purified according to the catalyst for exhaust gas clarification which uses noble metals, such as platinum (Pt), palladium (Pd), and a rhodium (Rh), as a catalyst component. Such a catalyst for exhaust gas clarification usually carries out the coat of the catalyst support, such as gamma-alumina, to honeycomb base materials, such as a product made from cordierite equipped with many cels, supports co-catalyst components, such as NOx occlusion material, by the further above-mentioned catalyst component and the case, and is constituted.

[0003] However, various kinds of amelioration has piled up to the clarification engine performance of such a catalyst for exhaust gas clarification for environmental protection. Made the cel consistency of a honeycomb base material increase, the touch area with the exhaust gas which the catalyst support by which a coat is carried out to a cell wall gives to a catalyst component was made to increase as one of the policies of this amelioration, and raising contacting efficiency with the exhaust gas of a catalyst component by it has been performed.

[0004]

[Problem(s) to be Solved by the Invention] However, it already being fairly increased by the cel consistency of a honeycomb base material, and making the number of cels increase further makes the rate of the cell wall cross section occupied in the cross section of exhaust gas passage, and the coat layer cross section of catalyst support increased considerably. For this reason, making a cel consistency increase further will increase the pressure loss of the exhaust gas which circulates the catalyst for exhaust gas clarification, and it will cause aggravation of fuel consumption. Moreover, the catalyst for exhaust gas clarification needs to be equal to mechanical works, such as an oscillation, over a long period of time.

[0005] By the way, plug stuffing of the cel was alternately carried out for the purpose of purifying previously the particulate contained in the exhaust gas of a diesel power plant in JP,9-94434,A, and these people have proposed the Wall flow mold exhaust gas clarifying filter with which exhaust gas penetrates the cell wall of an open pore, and flows. However, in this official report, it has not indicated special about the clarification engine performance in the catalyst for exhaust gas clarification of a negotiation type, pressure loss, and endurance.

[0006] Therefore, this invention aims at offering the catalyst for exhaust gas clarification which does not increase the pressure loss of the exhaust gas which flows the catalyst for exhaust gas clarification, and raises the exhaust gas clarification engine performance by raising contacting efficiency with the exhaust gas of a catalyst component, and is excellent also in endurance in the catalyst for exhaust gas clarification of a negotiation type.

[0007]

[Means for Solving the Problem] The above-mentioned object is used for the catalyst for exhaust gas clarification as the 1st mode. It is the catalyst support structure of the negotiation type which comes to carry out the coat of the catalyst support to a honeycomb base material. The coat of the catalyst support is carried

out the inside of the cell wall pore of a honeycomb base material, and on a cell wall front face. The amount of the catalyst support on the cell wall front face by which the coat was carried out is attained by the catalyst support structure characterized by being ten to 40 mass [ of the whole catalyst support ] %, and the coat layer of the catalyst support on a cell wall front face being the thickness of less than 100 micrometers.

[0008] Drawing 1 shows in model the sectional view seen from the flow direction of the exhaust gas of this catalyst support structure. As shown in drawing 1, the coat of a part of catalyst support, such as gamma-alumina, is carried out into the cell wall pore of a honeycomb base material, it constitutes some cell walls, the whole cell wall is covered, and the coat layer of catalyst support exists.

[0009] That is, the catalyst support structure of this invention makes a component the honeycomb base material which has pore in a cell wall, and has the coat layer of catalyst support to two fields, the inside of cell wall pore, and a cell wall front-face top. The coat layer of catalyst support is porosity, and since exhaust gas is circulated, the catalyst component supported by the catalyst support to a certain allowance thickness can demonstrate a catalyst function effectively. For this reason, the catalyst support within the cell wall from the top face of the coat layer of the catalyst support on a cell wall front face to this allowance thickness turns into catalyst support effective in exhaust gas clarification.

[0010] Therefore, the quantity of the amount equivalent to the catalyst support in the cell wall pore which fills allowance thickness can be made to be able to decrease from the coat layer on the front face of a cell wall, consequently the thickness of the coat layer on the front face of a cell wall can decrease, and passage of exhaust gas can be made large.

[0011] Moreover, in catalyst support existing in cell wall pore, the pore as a defective part of a honeycomb base material is laid underground, and the mechanical strength of a honeycomb base material is secured. Furthermore, since the catalyst support in cell wall pore gives the so-called anchor effect to the coat layer on the front face of a cell wall, the catalyst support of the coat layer on the front face of a cell wall can have the high endurance over omission by mechanical works, such as an oscillation, etc. as one in cell wall pore.

[0012] It is found out that it is about 100 micrometers and, for this reason, the allowance thickness as the effective above-mentioned catalyst support limits the thickness of the coat layer of the catalyst support on a cell wall front face to less than 100 micrometers by this invention. This thickness is less than 70 micrometers preferably. Moreover, the amount of the catalyst support on a cell wall front face is ten to 40 mass [ of the whole catalyst support ] %. If it is this range, the thickness of the coat layer on the above-mentioned front face of a cell wall can be decreased intentionally, and an anchor effect can also become remarkable. This range is ten to 30 mass % preferably.

[0013] Preferably, the cell wall of a honeycomb base material has 40 - 75% of porosity, and D50 pore diameter of 10-50 micrometers. When the porosity of a honeycomb base material and D50 pore diameter are in these range, the honeycomb base material is easy to carry out the coat of the catalyst support to the above-mentioned range, and can offer sufficient reinforcement united with the catalyst support by which the coat was carried out. Moreover, the pore of the cell wall of a honeycomb base material is a non-breakthrough substantially preferably. Even if the cell wall has remarkable pore by this, partial omission of a cell wall are controlled and high endurance can be demonstrated to mechanical works, such as an oscillation.

[0014] To the catalyst support structure of such this invention, a co-catalyst component like NO<sub>x</sub> occlusion material is supported by catalyst components, such as Pt, and the case, and the catalyst for exhaust gas clarification is constituted. Here, or the catalyst component and/or co-catalyst component ("a catalyst component etc. is called" below.) which are supported by the catalyst support in cell wall pore, the catalyst component supported by the catalyst support on a cell wall front face are substantially the same, it can be different and it can be determined by thermal resistance, such as the reactivity of the harmful matter which should be purified, and/or a catalyst component, etc.

[0015] For example, in the catalyst for exhaust gas clarification of the internal combustion engine with which exhaust gas mainly serves as a SUTOIKI ambient atmosphere, it is necessary to support noble metals, such as Pt, Pd, and Rh, as a catalyst component so that the three way component catalyst engine performance may fully be discovered. Moreover, to the exhaust gas of the internal combustion engine with which exhaust gas mainly serves as lean atmosphere, the exhaust gas clarification engine performance in which the catalyst for occlusion reduction type NO<sub>x</sub> clarification with which NO<sub>x</sub> occlusion material, such as a potassium (K) and barium (Ba), was supported in addition to these noble metals is high can be offered.

[0016] In such a catalyst for exhaust gas clarification, if Pt and/or Pd are supported to the catalyst support in cell wall pore and Rh is supported to the catalyst support on a cell wall front face, since thermal resistance is high as compared with Pt and Pd, Rh can have thermal resistance with a catalyst component high as a whole. Moreover, as for support of NO<sub>x</sub> occlusion material, such as K and Ba, supporting in cell wall pore

is desirable. Bypassing without NO<sub>x</sub> emitted from NO<sub>x</sub> occlusion material contacting a catalyst component by this can be controlled notably.

[0017] Moreover, it is desirable to support HC adsorption material to the catalyst support on a cell wall front face the making HC adsorb temporarily using HC adsorption material, such as a zeolite, by the time a catalyst warms up object.

[0018] The above-mentioned object is used for the catalyst for exhaust gas clarification as the 2nd mode. Are the catalyst support structure of the negotiation type which comes to carry out the coat of the catalyst support to a honeycomb base material, and the coat of the catalyst support is carried out the inside of the cell wall pore of a honeycomb base material, and on a cell wall front face, and it sets to the exhaust gas downstream of the catalyst support structure. The amount of the catalyst support on the cell wall front face by which the coat was carried out is ten to 40 mass [ of the whole catalyst support ] %, and the coat layer of the catalyst support on a cell wall front face is less than 100 micrometers in thickness, and it sets to the exhaust gas upstream of the catalyst support structure. The amount of the catalyst support in the cell wall pore by which the coat was carried out is attained by the catalyst support structure characterized by being more than 90 mass % of the whole catalyst support.

[0019] Drawing 2 shows in model the sectional view seen from the perpendicular direction of the flow of exhaust gas of the catalyst support structure of this 2nd mode. By the exhaust gas upstream, as shown in drawing 2 , although the exhaust gas downstream of the catalyst support structure is the same configuration as the catalyst support structure of the 1st above-mentioned mode, or the catalyst support coat layer on a cell wall front face exists only in few amount, it does not exist substantially but almost all catalyst support exists in cell wall pore.

[0020] The catalyst support structure of the 2nd mode is the exhaust gas upstream, exhaust gas passage becomes still larger and the pressure loss of exhaust gas declines rather than the 1st mode as a whole. And the catalyst support in the cell wall pore in the above-mentioned allowance thickness of the exhaust gas upstream and the downstream can turn into effective catalyst support like the 1st mode. To the catalyst support structure of this mode, a catalyst component etc. is supported like the 1st mode, and the catalyst for exhaust gas clarification is constituted.

[0021] In this mode, the catalyst support by which the coat was carried out is classifiable into three fields, the inside of the cell wall pore of the exhaust gas upstream, and the cell wall pore of the exhaust gas downstream, and a cell wall front-face top. The catalyst component from which each catalyst support of these fields differs, respectively although the same catalyst component etc. can be supported can also be supported.

[0022] For example, noble metals, such as NO<sub>x</sub> occlusion material and Pt, are supported to the catalyst support in the cell wall pore of the exhaust gas upstream and the downstream, the noble metals of a three way component catalyst are supported on the cell wall front face of the exhaust gas downstream, and the catalyst for occlusion reduction type NO<sub>x</sub> clarification is constituted. In this configuration, NO<sub>x</sub> by which occlusion was carried out to the NO<sub>x</sub> occlusion material in cell wall pore at the time of Lean operation is returned by HC and CO at the time of temporary rich operation, and superfluous HC and superfluous CO oxidize with the three way component catalyst on a cell wall front face to reduction of NO<sub>x</sub>. That is, since it is secured that superfluous HC and superfluous CO contact a three way component catalyst, the catalyst for occlusion reduction type NO<sub>x</sub> clarification to which the clarification engine performance of HC and CO was raised can be offered rather than the configuration using the conventional catalyst support structure. Moreover, NO<sub>x</sub> occlusion material can be supported in this way, and HC adsorption material can also be supported to the catalyst support on the cell wall front face of the exhaust gas downstream.

[0023] Here, after setting to manufacture the catalyst support structure of this invention and carrying out the coat of the catalyst support into the cell wall pore of a honeycomb base material, it is mentioned using the slurry containing ceramic fiber as the manufacture approach with desirable carrying out the coat of the catalyst support on the cell wall front face of a honeycomb base material. This reason is considered as follows.

[0024] If catalyst support is calcinated in case the coat of the catalyst support is carried out into the cell wall pore of a honeycomb base material, generally pore will arise by contraction of a catalyst support raw material etc. Therefore, if the coat of the catalyst component is carried out on a cell wall front face next, a part of catalyst component permeates into this pore. Here, if ceramic fiber is contained in a slurry, as shown in drawing 3 in model, this encroachment can be prevented and the catalyst support of the field the inside of cell wall pore and on a cell wall front face can be classified clearly. Therefore, when catalyst support differs from a catalyst component the inside of cell wall pore, and on a cell wall front face, this manufacture

approach is effective, and since this pore does so the operation which raises contact to the catalyst component and exhaust gas which were supported by the catalyst support in cell wall pore, it can raise the exhaust gas clarification engine performance.

[0025] Drawing 4 shows the catalyst support structure of the conventional technique in model. As shown in drawing 4, since the coat of the catalyst support is substantially carried out only on a cell wall front face, a coat layer becomes thick and it will cause buildup of the pressure loss of exhaust gas. Moreover, it originates in a thick coat layer, and the coat of the catalyst support is carried out thickly, and exhaust gas does not circulate substantially in the part of this corner in the part of the corner of a cel. For this reason, it not only causes buildup of pressure loss, but catalyst support and a catalyst component become useless and it becomes bringing about the unnecessary increment in the heat capacity of the catalyst for exhaust gas clarification further.

[0026] It is remarkably mitigated by that the problem of such a conventional technique has a thin coat layer on a cell wall front face in the catalyst support structure of this invention, futility in the corner of a cel, such as catalyst support and a catalyst component, is also canceled, and the unnecessary increment in this heat capacity that originates vainly is also canceled. Therefore, early warming-up nature can be improved and it can be suitably used also as a start-up catalyst arranged near the engine exhaust port.

[0027] In addition to the dissolution of the problem of such a conventional technique, it can contribute to improvement in the exhaust gas clarification engine performance because this invention raises the endurance of the coat layer of catalyst support as mentioned above and carries out clear [ of the field partition of catalyst support ]. In addition, in this invention, the configuration of the cel of a honeycomb base material can be the usual square, and can be the polygon of the hexagon shown in drawing 5, and others. It is for bringing about the increment in the amount of support of catalyst support and a catalyst component that make it into a polygon and its circumference of the cross section of a cell wall increases since this invention transposes some cell walls to catalyst support.

[0028]

[Embodiment of the Invention] the catalyst support structure of the negotiation type of this invention -- the 1st voice -- it sets like and catalyst support carries out a coat the inside of the cell wall pore of a honeycomb base material, and on a cell wall front face -- having -- the amount of the catalyst support on the cell wall front face by which the coat was carried out -- ten to 40 mass [ of the whole catalyst support ] % -- it is ten to 30 mass %, and less than 100 micrometers of coat layers of the catalyst support on a cell wall front face are less than 70 micrometers in thickness preferably.

[0029] What consists of a multiple oxide like zirconia-Seria [ besides an alumina, a zirconia, and oxide like Seria ] and alumina-Seria-zirconia and Seria-zirconia-ytria and zirconia-calcia as catalyst support is suitably usable.

[0030] What consists of cordierite, an alumina, a zirconia, and a ceramic ingredient with thermal resistance like silicon carbide as a honeycomb base material is suitably usable. what has the cel of a large number to which ends carried out opening of this honeycomb base material is used, and the cel consistency of a honeycomb base material is limited especially in this invention -- it is not necessary to have -- about 200 -- the thing of semi-gross density like cels / square inch, and 1000 cel / square inch -- the thing of high density can be used as mentioned above.

[0031] Preferably, although the cell wall of this honeycomb base material has 40 - 75% of porosity, and D50 pore diameter of 10-50 micrometers "The porosity of a cell wall" in this invention means the porosity measured according to the method of mercury penetration using the mercury porosimeter. With "D50 pore diameter of a cell wall" The accumulation volume in the pore diameter distribution measured according to the approach using this mercury porosimeter means the pore diameter which is 50%.

[0032] Preferably, the pore which exists in the cell wall of a honeycomb base material is a non-breakthrough substantially, and it means that at least 90% has not penetrated both the walls of a cell wall at least 70% with an individual number average as the vocabulary "it is a non-breakthrough substantially" in this invention in the pore observed in the cross section of the cell wall of a direction vertical to the flow direction of exhaust gas. It can be evaluated by observing the cross section of a cell wall whether the pore of this cell wall is a breakthrough.

[0033] The catalyst support structure of this invention by which the coat of the catalyst support was carried out to such a honeycomb base material and it can be manufactured as follows, for example. A honeycomb base material can carry out extrusion molding of the ceramic raw material compound using honeycomb metal mold, and can obtain it by subsequently performing desiccation and baking. If the ingredient of destruction-by-fire nature with which particle diameter was adjusted into for example, the raw material

compound is blended by the specified quantity here, it is possible to control the porosity of the cell wall of a honeycomb base material and D50 pore diameter which are obtained in the range of target.

[0034] As an ingredient of this destruction-by-fire nature, for example, a graphite particle, carbon black, a carbon fiber chop, etc. are mentioned, and these have that comparatively easily available by which particle diameter and die length were adjusted to the range of desired.

[0035] Moreover, substantially, using comparatively narrow graphite particle or carbon black of particle size distribution, the pore of a cell wall can add a dispersant as occasion demands, can prepare a raw material compound so that these destruction-by-fire nature ingredients may not condense in a compound, and it can obtain the honeycomb base material of a non-breakthrough by subsequently performing the above-mentioned extrusion molding, and desiccation and baking preferably. Moreover, the honeycomb base material similarly equipped with the non-breakthrough prolonged in single dimension can be obtained by using a carbon fiber chop shorter than the thickness of a cell wall.

[0036] Thus, the coat of the catalyst support is carried out to the obtained honeycomb base material. This coat can be performed as follows, for example. A slurry is prepared using powder, such as the above-mentioned alumina, a zirconia, and the Seria-zirconia, a honeycomb base material is immersed in this slurry, and impregnation of the slurry is carried out. Or impregnation of the slurry is compulsorily carried out to a honeycomb base material by immersing a honeycomb base material in this slurry, and decompressing a slurry, or giving mechanical oscillation, such as a supersonic wave, to a honeycomb base material.

[0037] Subsequently, the honeycomb base material which sank in this slurry can be dried and calcinated, and the coat of the catalyst support can be carried out. Here, in order to carry out the coat of the catalyst support into cell wall pore, when catalyst support prepares the slurry which has D90 particle diameter which is less than D50 pore diameter of the cell wall of a honeycomb base material and, subsequently to a honeycomb base material, carries out the wash coat of this slurry in a slurry, catalyst support can be arranged comparatively easily in the pore of the cell wall of a honeycomb base material.

[0038] "D90 particle diameter" of the slurry of this catalyst support means the particle diameter of 90% accumulation mass of the catalyst support in the prepared slurry. Here, although dynamic light scattering, the optical diffraction scattering-about method, the gas-chromatography method, a sedimentation method, etc. are mentioned to the measuring method of the grain size in a slurry, "D90 particle diameter" in this invention is the value measured by the optical diffraction scattering-about method. D90 particle diameter of the catalyst support in a slurry can be reduced to desired level by addition of the time amount which mills a slurry, reinforcement, or a dispersant.

[0039] On a cell wall front face, the coat layer of catalyst support exists by the thickness of less than 100 micrometers. After the coat layer on this front face can be formed in the coat layer and coincidence in cell wall pore or carries out a coat into cell wall pore, it can also form the coat layer on a cell wall front face. In this case, the coat layer the inside of pore and on a front face can also be made into different catalyst support with the target catalyst engine performance. Means, such as accommodation of the viscosity of a slurry which carries out a wash coat, or a count of a wash coat, can adjust the thickness of the coat layer on a cell wall front face.

[0040] In the 2nd mode, the coat of the catalyst support is carried out the inside of the cell wall pore of a honeycomb base material, and on a cell wall front face, and it sets the catalyst support structure of the negotiation type of this invention to the exhaust gas downstream of the catalyst support structure. The amount of the catalyst support on the cell wall front face by which the coat was carried out is ten to 40 mass [ of the whole catalyst support ] %, and the coat layer of the catalyst support on a cell wall front face is less than 100 micrometers in thickness, and it sets to the exhaust gas upstream of the catalyst support structure. The amount of the catalyst support in the cell wall pore by which the coat was carried out is more than 90 mass % of the whole catalyst support.

[0041] In the 2nd mode, although the exhaust gas downstream of the catalyst support structure is the catalyst support structure of the 1st mode, as for the exhaust gas upstream, almost all catalyst support exists in cell wall pore. Using means, such as carrying out impregnation of the slurry to a honeycomb base material compulsorily as occasion demands for example, as mentioned above, such the catalyst support structure supports catalyst support in the cell wall pore of a honeycomb base material, subsequently to a slurry, can dip the lower part of the honeycomb base material, and can prepare it by attracting and carrying out the wash coat of the slurry to predetermined height etc.

[0042] Thus, co-catalyst components, such as NO<sub>x</sub> occlusion material, are supported by a catalyst component and the need, and the catalyst for exhaust gas clarification is constituted by the prepared catalyst support structure of the 1st and the 2nd mode. Eight groups, 1B group who contain 3A - 7A group of the



periodic table, and noble metals as a catalyst component, The transition metals containing f-block element are suitably usable. And manganese (Mn), Iron (Fe), cobalt (Co), nickel (nickel), copper (Cu), an yttrium (Y), A zirconium (Zr), niobium (Nb), molybdenum (Mo), a hafnium (Hf), A tantalum (Ta), a tungsten (W), a lanthanum (La), a cerium (Ce), Noble metals, such as PURASEOJIUMU (Pr), neodymium (Nd) and platinum (Pt), gold (Au), palladium (Pd), a ruthenium (Ru), and a rhodium (Rh), are illustrated. Preferably They are at least one sort of transition metals chosen from Mn, Fe, Co, nickel, Cu, Pt, Au, Pd, Ru, and Rh, and at least one sort of noble metals more preferably chosen from Pt, Pd, and Rh.

[0043] As a co-catalyst component, what has NO<sub>x</sub> occlusion ability, such as a lithium (Li), a potassium (K), calcium (calcium), and barium (Ba), and the thing which has HC absorbing power like specific zeolite ZSM-5 are illustrated. These catalyst components and co-catalyst components can be supported to catalyst support using various kinds of nitrate, acetate, chlorides, complexes, or powder slurries etc. with the usual means by an evaporation-to-dryness method, settling, the adsorption process, the ion-exchange method, the reduction depositing method, etc.

[0044] Here, when the catalyst component supported by the catalyst support in cell wall pore, the catalyst component supported by the catalyst support on a cell wall front face are different, the support location of a catalyst component can be adjusted by supporting a catalyst component etc. to the catalyst support, after carrying out the coat of the catalyst support into cell wall pore, and supporting a catalyst component etc. to the catalyst support, after, carrying out the coat of the catalyst support subsequently to a cell wall front-face top. Hereafter, an example explains this invention more concretely.

[0045]

[Example] As it was one or less example, the catalyst support structure of this invention by which the coat of the catalyst support was carried out the inside of cell wall pore and on the cell wall front face was manufactured. The graphite particle 10 mass section whose D50 particle diameter is 10 micrometers as the methyl cellulose and the ostomy material of 30 mass sections as the water of the 300 mass sections and a binder was added to these, these were kneaded with the kneading machine for 2 hours, using the kaolin of the 350 mass sections, the talc of the 300 mass sections, and the alumina of the 100 mass sections as an oxide raw material, and the raw material compound of a honeycomb base material was prepared.

[0046] Extrusion molding of this compound was carried out, it calcinated in the 1450-degree C atmospheric-air ambient atmosphere for 20 hours, and the honeycomb base material of 150 micrometers in diameter [ of 80mm ] x die length of 95mm and cell wall thickness and a cordierite presentation of cel consistency 400 cel / square inch was obtained. As a result of measuring the pore condition of the obtained honeycomb base material according to a method of mercury penetration using the mercury porosimeter (auto pore 9420 by the microphone ROMERI tick company), D50 pore diameter of porosity was 30 micrometers 60%.

[0047] Subsequently, catalyst support was supported to this honeycomb base material as follows. The ion exchange water of the 200 mass sections was added to the gamma-alumina (specific surface area: about 150m<sup>2</sup>/g, D50 particle-diameter:20micrometer) of 50 mass sections, and the Seria-zirconia (specific surface area: about 100m<sup>2</sup>/g, mole ratio of CeO<sub>2</sub>/ZrO<sub>2</sub>=1/1) of 50 mass sections, and it mixed over 50 hours with the ball mill.

[0048] 2 micrometers and D90 particle diameter of D50 particle diameter of this mixed powder were 15 micrometers. In addition, ion exchange water was further added in the amount from which the solid content of alumina sol becomes 3% on the basis of sum total mass with mixed powder about alumina sol (product A-200 made from the Nissan chemistry) to this mixed powder, and the catalyst support slurry of 25% of solid content was obtained to it. Measurement of D50 particle diameter and D90 particle diameter was performed by the optical diffraction scattering-about method (Oliver LA- 920).

[0049] Subsequently, after the above-mentioned honeycomb base material was immersed in this catalyst support slurry, with high voltage air, the catalyst support slurry was blown off slightly, it calcinated in the 400-degree C atmospheric-air ambient atmosphere for 1 hour, and the coat layer of 80g catalyst support was formed in the honeycomb base material (160g catalyst support / 1l. support).

[0050] Subsequently, this honeycomb base material was again immersed in the above-mentioned catalyst support slurry, with high voltage air, the catalyst support slurry was blown off slightly, it calcinated in the 400-degree C atmospheric-air ambient atmosphere for 1 hour, the coat of the 40g catalyst support was carried out to the honeycomb base material (80g catalyst support / 1l. support), and the catalyst support structure of this invention was obtained. The coat of the catalyst support of 35 mass % of the whole catalyst support was carried out to this catalyst support structure on the cell wall front face. In addition, this amount of coats is the value which cut the catalyst support structure, shaved off the catalyst support located in the outside of a cell wall, and was calculated from that mass and the mass of a cell wall.

[0051] As it was one or less example of a comparison, the catalyst support structure of the example of a comparison by which the coat of much catalyst support was carried out on the cell wall front face was manufactured. As a raw material compound of the honeycomb base material in an example 1, it replaced with the graphite particle 10 mass section, and the raw material compound was prepared like the example 1 except having considered as the graphite particle 2 mass section. Subsequently, like the example 1, after carrying out extrusion molding of this compound, it calcinated and the honeycomb base material of a cordierite presentation with diameter [ of 80mm ] x die length of 95mm, an inch [ cel consistency 400 cel / square inch ], and a cell wall thickness of 150 micrometers was obtained. The pore condition of the obtained honeycomb base material was 7 micrometers in 38% of porosity, and D50 pore diameter.

[0052] Subsequently, the mixture of gamma-alumina / Seria-zirconia / ion-exchange-water =50/50/200 was prepared with the mass ratio like the example 1. However, 15 micrometers and D90 particle diameter were stopped for D50 particle diameter to 30 micrometers, having used grinding time amount by the ball mill as 1 hour. The catalyst support slurry was created like the example 1, the coat of the catalyst support was carried out to the honeycomb base material 2 times, the coat of the 120g catalyst support containing gamma-alumina and the Seria-zirconia was formed, and the catalyst support structure of the example of a comparison was obtained from this mixture. The coat of the 90 mass % of the whole catalyst support was carried out to this catalyst support structure on the cell wall front face.

[0053] - The rate of coat exfoliation under the following exfoliation acceleration conditions estimated the mechanical strength of the catalyst support structure of the mechanical-strength assessment-example 1 of catalyst support, and the example 1 of a comparison. After drying at 250 degrees C for 4 hours, weighing capacity of each of the catalyst support structure was carried out. Subsequently, the catalyst support structure was dipped into water, and it put to the supersonic wave with a frequency of about 35kHz for 1 minute by output 100W, and subsequently, after blowing away attached groundwater slightly through application-of-pressure air in the cel of the catalyst support structure and drying at 250 degrees C for 4 hours, weighing capacity of the catalyst support structure was carried out.

[0054] The mass which decreased from the difference of this weight and the first weight was calculated, division of it was carried out with the mass of the catalyst support on a honeycomb base material, and the acquired value was made into the rate of coat exfoliation. Consequently, the rate of coat exfoliation was 0.5% in the example 1 of a comparison 0.03% in the example 1.

[0055] - The differential pressure before and behind the catalyst support structure was measured, circulating air by the flow rate for 7m<sup>3</sup>/to each catalyst support structure of the measurement-example 1 of pressure loss, and the example 1 of a comparison. Consequently, in the example 1, they were 2.1kPa(s) in 1.7kPa(s) and the example 1 of a comparison.

[0056] As it was two or less example, the catalyst for exhaust gas clarification with which Pt, Ba, and K were supported by the catalyst support structure of this invention was manufactured. The coat layer of the 80g catalyst support which contains gamma-alumina and the Seria-zirconia using the catalyst support slurry prepared like the example 1 at the mass ratio from the mixture of gamma-alumina / Seria-zirconia / ion-exchange-water =50/50/200 in the cell wall pore with a% [ of porosity ] of 60 and D50 pore diameter of 30 micrometers of a honeycomb base material by diameter [ of 80mm ] x die length of 95mm prepared like the example 1 was formed.

[0057] Subsequently, sink into this coat layer and a dinitrodiammine platinum complex water solution is calcinated in a 400-degree C atmospheric-air ambient atmosphere after desiccation in it for 1 hour. Support 1.0g [ per 1l. of honeycomb base materials ] Pt, and further, sink in and the water solution which dissolved barium acetate and potassium acetate in this coat layer is calcinated in a 400-degree C atmospheric-air ambient atmosphere after desiccation for 1 hour. 0.2 mols [ per 1l. of honeycomb base materials ] Ba and 0.1 mols K were supported.

[0058] Subsequently, as an ingredient of catalyst support, the alumina fiber with a diameter [ of about 1 micrometer ] x die length of about 50 micrometers was added on the average, the mixture of gamma-alumina / Seria-zirconia / alumina fiber / ion-exchange-water =50/50/10/200 was prepared with the mass ratio, and the catalyst support slurry was prepared like the example 1 from this mixture. Subsequently, after dipping above Pt and the honeycomb base material bottom which supported Ba and K in this catalyst support slurry, with high voltage air, the catalyst support slurry was blown off slightly, it calcinated in the 400-degree C atmospheric-air ambient atmosphere after desiccation for 1 hour, and the coat layer of 4g catalyst support was formed in 20mm of honeycomb base material bottoms.

[0059] Subsequently, the dinitrodiammine platinum complex water solution was sunk into the coat layer of this bottom, it calcinated in the 400-degree C atmospheric-air ambient atmosphere after desiccation for 1

hour, and 2.0g [ per 1l. of honeycomb base materials ] Pt was supported. According to the above process, the coat of the catalyst support on a cell wall front face was carried out only to the downstream of exhaust gas, Pt was supported to the whole catalyst support, Ba and K were supported only to the catalyst support in cell wall pore, and the catalyst support on a cell wall front face acquired the catalyst for exhaust gas clarification of this invention containing an alumina fiber.

[0060] the example 1 of reference -- the catalyst for exhaust gas clarification was manufactured like the example 1 except having supported Ba and K to the whole catalyst support. Like the example 2, after forming the 80g coat layer of gamma-alumina and the Seria-zirconia in a honeycomb base material, the coat layer of the 40g catalyst support which contains gamma-alumina, the Seria-zirconia, and an alumina fiber in 20mm of honeycomb base material bottoms was formed like the example 2.

[0061] Subsequently, sink a dinitrodiammine platinum complex water solution into these whole coat layer as well as an example 2, and it calcinates in a 400-degree C atmospheric-air ambient atmosphere after desiccation for 1 hour. Support 1.5g [ per 1l. of honeycomb base materials ] Pt, and further, sink in and the water solution which dissolved barium acetate and potassium acetate in this coat layer is calcinated in a 400-degree C atmospheric-air ambient atmosphere after desiccation for 1 hour. 0.2 mols [ per 1l. of honeycomb base materials ] Ba and 0.1 mols K were supported.

[0062] As it was three or less example, the catalyst for exhaust gas clarification with which Pt, Pd, and Rh were supported by the catalyst support structure of this invention was manufactured. By diameter [ of 80mm ] x die length of 95mm prepared like the example 1, the catalyst support slurry was prepared with the mass ratio like the example 1 from the mixture of gamma-alumina / Seria-zirconia / ion-exchange-water =50/50/200 in the cell wall pore with a% [ of porosity ] of 60, and D50 pore diameter of 30 micrometers of a honeycomb base material, and the coat layer of the 80g catalyst support containing gamma-alumina and the Seria-zirconia was formed.

[0063] Subsequently, it sank into this coat layer, the palladium-chloride water solution was calcinated in the 400-degree C atmospheric-air ambient atmosphere after desiccation in it for 1 hour, and 1.0g [ per 1l. of honeycomb base materials ] Pd was supported in it.

[0064] Subsequently, as an ingredient of catalyst support, the alumina fiber with a diameter [ of about 1 micrometer ] x die length of about 50 micrometers was added on the average, the mixture of gamma-alumina / Seria-zirconia / alumina fiber / ion-exchange-water =50/50/10/200 was prepared with the mass ratio, and the catalyst support slurry was prepared like the example 1 from this mixture. Subsequently, after dipping the whole honeycomb base material which supported the above-mentioned Pd in this catalyst support slurry, the slurry was slightly blown off with high voltage air, it calcinated in the 400-degree C atmospheric-air ambient atmosphere after desiccation for 1 hour, and the coat layer of 20g catalyst support was formed on the cell wall front face.

[0065] Subsequently, the dinitrodiammine platinum complex and the nitric-acid rhodium water solution were sunk into this coat layer, it calcinated in the 400-degree C atmospheric-air ambient atmosphere after desiccation for 1 hour, and 0.5g [ per 1l. of honeycomb base materials ] Pt and 0.5g Rh were supported. According to the above process, the coat of the catalyst support on a cell wall front face was carried out to the whole catalyst support structure, Pd was supported in cell wall pore, Pt and Rh were supported on the cell wall front face, and the catalyst support on a cell wall front face acquired the catalyst for exhaust gas clarification of this invention containing an alumina fiber.

[0066] As it was two or less example of reference, Pd was supported in cell wall pore and Pt and Rh manufactured the catalyst for exhaust gas clarification like the example 1 except having supported on the cell wall front face. By diameter [ of 80mm ] x die length of 95mm prepared like the example 1, the catalyst support slurry was prepared with the mass ratio like the example 1 from the mixture of gamma-alumina / Seria-zirconia / ion-exchange-water =50/50/200 in the cell wall pore with a% [ of porosity ] of 60, and D50 pore diameter of 30 micrometers of a honeycomb base material, and the coat layer of the 80g catalyst support containing gamma-alumina and the Seria-zirconia was formed.

[0067] Subsequently, it sank into this coat layer, the dinitrodiammine platinum complex and the nitric-acid rhodium water solution were calcinated in the 400-degree C atmospheric-air ambient atmosphere after desiccation in it for 1 hour, and 0.5g [ per 1l. of honeycomb base materials ] Pt and 0.5g Rh were supported in it. Subsequently, as an ingredient of catalyst support, the alumina fiber with a diameter [ of about 1 micrometer ] x die length of about 50 micrometers was added on the average, the mixture of gamma-alumina / Seria-zirconia / alumina fiber / ion-exchange-water =50/50/10/200 was prepared with the mass ratio, and the catalyst support slurry was prepared like the example 1 from this mixture.

[0068] Subsequently, after dipping the whole honeycomb base material which supported above Pt and Rh in

this catalyst support slurry, the slurry was slightly blown off with high voltage air, it calcinated in the 400-degree C atmospheric-air ambient atmosphere after desiccation for 1 hour, and the coat layer of 20g catalyst support was formed on the cell wall front face. Subsequently, the palladium-chloride water solution was sunk into this coat layer, it calcinated in the 400-degree C atmospheric-air ambient atmosphere after desiccation for 1 hour, and 1.0g [ per 1l. of honeycomb base materials ] Pd was supported.

[0069] - each catalyst of the assessment (1)-example 2 of the catalyst engine performance and the example 1 of reference has been arranged to exhaust gas clarification performance-evaluation equipment, and after pretreating by having circulated 500-degree C rich gas for 10 minutes for each catalyst and, circulating rich gas and lean gas subsequently to the every alternation during 2 minutes for it, in space-velocity 100000h-1, the rate of NOX clarification in 500-degree C lean gas was measured.

Lean-gas presentation: NO:800ppm+C3H6:2400ppm+CO2:11.0%+CO:700ppm+O2:7.0%+H2O:3.0% (remainder: N2)

Rich-gas presentation: NO:100ppm+C3H6:6700ppm+CO2:11.0%+CO:5900ppm+O2:0%+H2O:3.0% (remainder: N2)

In the measurement result of this rate of NOX clarification, and the example 2, it was 62% in the example 1 of reference 75%.

[0070] - The container made from stainless steel was equipped with each catalyst of the assessment (2)-example 3 of the catalyst engine performance, and the example 2 of a comparison, it has been arranged in the exhaust manifold latter part of a gasoline engine with a displacement of 1l., and the durable processing which puts to the exhaust gas ambient atmosphere of SUTOIKI where the inlet gas temperature of a catalyst is 850 degrees C for 50 hours was presented with it. Subsequently, each catalyst after this durable processing has been arranged under an exhaust manifold, the engine was operated by 2000rpm, and the temperature from which the rate of HC clarification becomes 50% was measured. Consequently, in the example 3, it was 390 degrees C in 320 degrees C and the example 2 of a comparison.

[0071]

[Effect of the Invention] The pressure loss of exhaust gas is low and the exhaust gas clarification engine performance can offer the catalyst for exhaust gas clarification with high endurance highly.

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[Translation done.]

## \* NOTICES \*

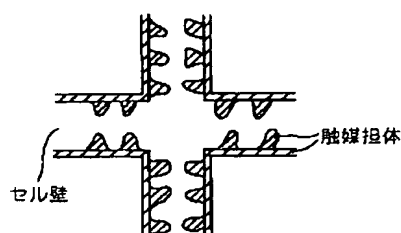
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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## DRAWINGS

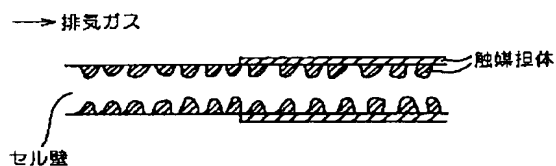
## [Drawing 1]

図1 本発明の触媒担体構造体のモデル図



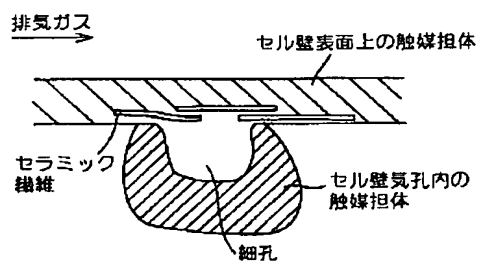
## [Drawing 2]

図2 本発明の触媒担体構造体のモデル図



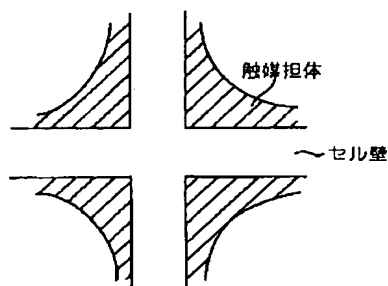
## [Drawing 3]

図3 本発明の触媒担体構造体のモデル図



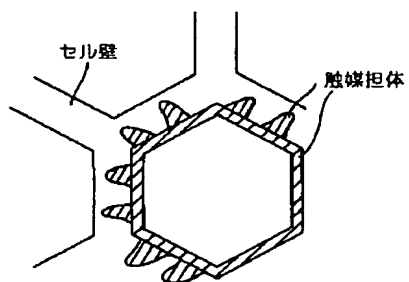
## [Drawing 4]

図4 従来技術の触媒担体構造体のモデル図



## [Drawing 5]

図 5 本発明の触媒担体構造体のモデル図



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[Translation done.]